Abstract No. kadu273
Structure and Bonding in Diammonium Terephthalates
J.A. Kaduk (BP Chemicals)
Beamline(s): X3B1

Introduction: Many billions of pounds of aromatic carboxylic acids - principally terephthalic acid, but also isophthalic acid and other compounds - are produced annually by homogeneous catalytic oxidation. Just as diammonium terephthalate [1] has proven to be a useful starting material for the preparation of metal terephthalate complexes, diammonium isophthalate serves as a reagent for the preparation of isophthalate salts. Comparison of the crystal structures of diammonium phthalate, isophthalate, and terephthalate in association with quantum chemical calculations provides insight into the bonding in these hydrogen-bonded solids.

Methods and Materials: Diammonium isophthalate was prepared by a gas-solid reaction between ammonia vapor and solid commercial isophthalic acid [2]. The powder diffraction pattern could be indexed on a *C*-centered monoclinic unit cell having a = 12.55654(4), b = 6.76445(3), c = 11.09806(6) Å, $ß$ = 110.2211(3)E, V = 884.553(7) Å^3, and Z = 4. The structure was solved in space group *Cc* using Monte Carlo simulated annealing techniques as implemented in the STRUCTURE_SOLVE module of InsightII [3], and refined in the true space group *C2/c* using GSAS [4]. Quantum chemical geometry optimizations of the three structures were carried out (fixed lattice parameters) at the CGA-PW91 level of theory using CASTEP [5].

Results: The final refinement of 49 variables using 11009 observations yielded the residuals *wRp* = 0.1200, *Rp* = 0.0832, $R(F^2)$ = 0.1119, $R(F)$ = 0.1146, and X^2 = 3.719; the agreement of the observed and calculated patterns (Fig. 1) is excellent. The structure (Fig. 2) consists of alternating layers of 1,3-benzenedicarboxylate anions and ammonium cations. The crystal structure is dominated by the parallel packing of aromatic rings and hydrogen bonding. Each carboxyl oxygen acts as a hydrogen bond acceptor to two ammonium hydrogens, and each ammonium hydrogen participates in a hydrogen bond. The hydrogen bond distances, angles, and overlap populations indicate that the hydrogen bonds are strong.

The density (1.503 gm/mL) of diammonium isophthalate (*meta*) is “normal”, while those of the phthalate (*ortho*) and terephthalate (*para*) salts are much lower (1.348 and 1.392 gm/mL, respectively). The quantum calculations quantify the balance between conformational energy differences and hydrogen bond energies, and explain the relative energies of the three salts. Such calculations also provide a practical way of locating the hydrogen atoms in structures derived *ab initio* using X-ray powder data.

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References:
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[5]. V. Milman, B. Winkler, J.A. White, C.J. Pickard, M.C. Payne, E.V. Akhmatskaya, and R.H. Nobes, *Int. J. Quant. Chem.*, **77**, 895-910 (2000).

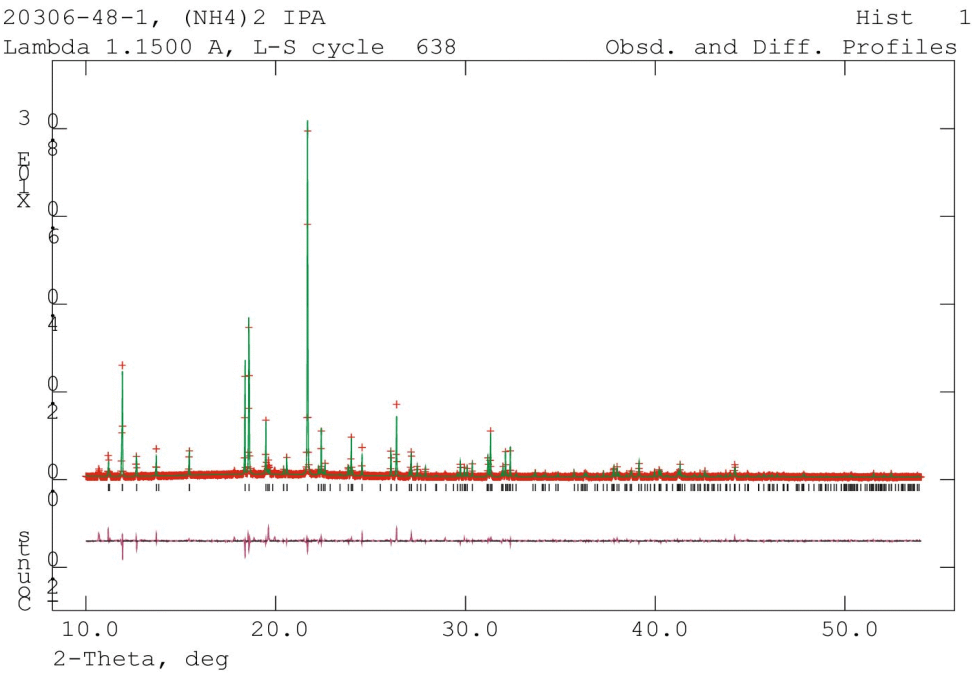

Figure 1. Observed, calculated, and difference patterns of diammonium isophthalate.

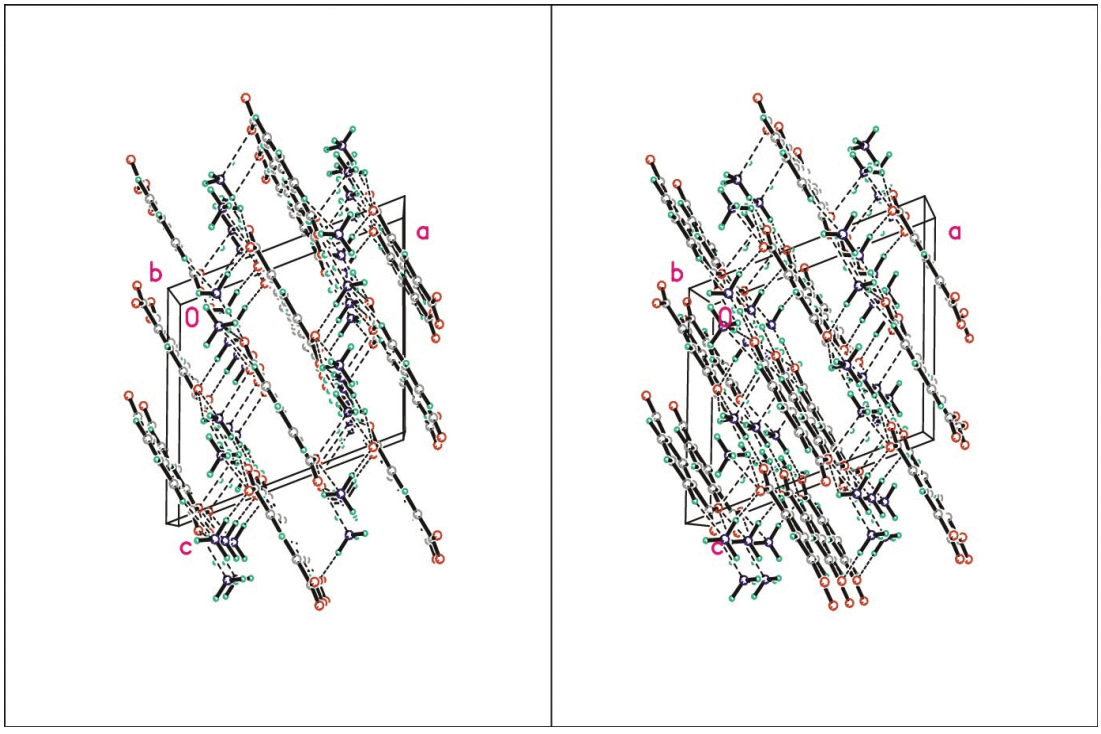

Figure 2. Stereo view of the crystal structure of diammonium isophthalate, down the monoclinic *b*-axis.